



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 848 077 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
12.03.2003 Bulletin 2003/11

(51) Int Cl.7: C23C 4/10, F02C 7/00

(21) Application number: 97310056.3

(22) Date of filing: 12.12.1997

(54) Thermal barrier coating systems and materials

Wärmesperrsichtsysteme und -materialien

Systèmes et matériaux de revêtement comme barrière thermique

(84) Designated Contracting States:
CH DE FR GB LI NL

(74) Representative: Hall, Matthew Benjamin
Frank B. Dehn & Co.
179 Queen Victoria Street
London EC4V 4EL (GB)

(30) Priority: 12.12.1996 US 764419

(56) References cited:
WO-A-98/26110 GB-A- 1 176 687
US-A- 3 954 512

(43) Date of publication of application:
17.06.1998 Bulletin 1998/25

• DATABASE WPI Section Ch, Week 9109,
Derwent Publications Ltd., London, GB; Class
L03, AN 91-063347, XP002900014 & JP 03 013 599
A (NIPPON STEEL CORP)

(73) Proprietor: UNITED TECHNOLOGIES
CORPORATION
Hartford, CT 06101 (US)

(72) Inventor: Maloney, Michael J.
Port St. Lucie, Florida 34983 (US)

EP 0 848 077 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] This invention relates to a class of ceramic materials for thermal barrier coatings, to thermal barrier coatings made of such materials, and to metallic parts having such thermal barrier coatings. The thermal barrier coatings have particular utility in gas turbine engines. The ceramic materials are a family of ceramics having a pyrochlore structure.

[0002] Gas turbine engines are well developed mechanisms for converting chemical potential energy, in the form of fuel, to thermal energy and then to mechanical energy for use in propelling aircraft, generating electric power, pumping fluids etc. At this time the major available avenue for improved efficiency of gas turbine engines appears to be the use of higher operating temperatures. However the metallic materials used in gas turbine engines are currently very near their upper limits of thermal stability. In the hottest portion of modern gas turbine engines, metallic materials are used at gas temperatures above their melting points. They survive because they are air cooled. But excessive air cooling reduces engine efficiency.

[0003] Accordingly, there has been extensive development of thermal barrier coatings for use with cooled gas turbine aircraft hardware. By using a thermal barrier coating, the amount of cooling air required can be substantially reduced.

[0004] Such coatings are invariably based on ceramics; mullite, alumina, etc. have been proposed but zirconia is the current material of choice. Zirconia must be modified with a stabilizer to preserve its cubic crystal structure at elevated temperatures, typical stabilizers include yttria, calcia, ceria and magnesia.

[0005] Generally speaking, metallic materials have coefficients of thermal expansion which exceed those of ceramic materials, consequently one of the problems that must be addressed in the development of successful thermal barrier coatings is to match the coefficient of thermal expansion of the ceramic material to the metallic substrate so that upon heating, when the substrate expands, the ceramic coating material does not crack. Zirconia has a high coefficient of thermal expansion and this is a primary reason for the success of zirconia as a thermal barrier material on metallic substrates.

[0006] Thermal barrier coatings have been deposited by several techniques including thermal spraying (plasma, flame and HVOF), sputtering and electron beam physical vapor deposition (EBPVD). Of these techniques, electron beam physical vapor deposition is currently a preferred technique for demanding applications because it produces a unique coating structure. Electron beam physical vapor deposited ceramic materials, when applied according to certain parameters, have a columnar grain microstructure consisting of small columns separated by gaps which extend into the coating. These gaps allow substantial substrate expansion without coating cracking and/or spalling-see US patent 4,321,311. According to US patent 5,073,433 a similar structure (comprising segmentation cracks), although on a larger scale, can be obtained by plasma spray techniques.

[0007] Despite the success with the current use of electron beam physical vapor deposited zirconia base coatings there is a continuing desire for improved coatings which exhibit superior thermal insulation capabilities, especially improved insulation capabilities when normalized for coating density. Weight is always a critical factor when designing gas turbine engines, particularly in rotating parts. Ceramics thermal barrier coatings are not load supporting materials, consequently they add weight without increasing strength. There is a strong desire for a ceramic thermal barrier material which adds the minimum weight while providing the maximum thermal insulation capability. In addition there are obviously the normal desires for long life, stability, economy etc.

[0008] Although this coating was developed for application in gas turbine engines, the invention clearly has utility in other applications where high temperatures are encountered such as furnaces.

[0009] The essence of the present invention arises from the discovery that a class of ceramic materials has great utility as thermal barrier coatings on metallic substrates. These materials have a pyrochlore crystal structure.

[0010] Ceramic materials having a pyrochlore crystal structure have been used previously in the field of electricity generation and electroplating where highly corrosive environments are encountered. For example, JP-A-03/013599 discloses the use of several pyrochlore-type structures as an alternative to a conventional lead insoluble electrode. GB-A-1176687 discloses the use of pyrochlore materials for use in the construction of or for lining vessels and pipes associated with a magnetohydrodynamic generator plant. US-A-3954512 suggests a range of pyrochlore-microlite minerals as a coating for use as components in electrical power plants.

[0011] It is also known from WO-A-98/26110 (which is prior art for the purposes of Article 54(3) EPC) to provide a thermal barrier coating comprising a perovskite or pyrochlore crystal structure. Suggested materials include lanthanum-hafnium ($La_2Hf_2O_7$), lanthanum-zirconate ($La_2Zr_2O_7$), aluminium-hafnium ($Al_2Hf_2O_7$), cerium-hafnium ($Ce_2Hf_2O_7$), cerium-zirconate ($Ce_2Zr_2O_7$), aluminium-cerium ($Al_2Ce_2O_7$) and lanthanum-cerium ($La_2Ce_2O_7$).

[0012] Thus, viewed from a first aspect, the present invention provides a metallic article comprising a metallic substrate, said substrate having a ceramic coating which has a cubic pyrochlore structure of formula $A_2B_2O_7$, wherein the A constituent consists essentially of Gd, and single phase mixtures of Gd with La and/or Y, and the B constituent is selected from Hf, Ti, Zr, and single phase mixtures thereof.

[0013] Viewed from a second aspect, the present invention provides a method of thermally insulating a metallic substrate which comprises applying a thermal barrier layer in the form of a ceramic coating to at least a portion of said

substrate by electron beam physical vapor deposition or thermal spray deposition, the ceramic coating having a cubic pyrochlore structure of formula $A_2B_2O_7$, wherein the A constituent consists essentially of Gd, and single phase mixtures of Gd with La and/or Y, and the B constituent is selected from the group comprising Hf, Ti, Zr and single phase mixtures thereof.

5 [0014] In a preferred embodiment, the metallic article is a superalloy gas turbine component which operates in an environment with gas temperatures in excess of 1,000°C, said component having internal cooling passages and the pyrochlore coating being located to reduce heat flow into said component.

10 [0015] The term pyrochlore is used to identify an ore of tantalum found in Canada. The term more generally describes a ceramic structure of the composition $A_2B_2O_7$ where A can have valence of 3+ or 2+ and B can have a valence of 4+ or 5+ and wherein the sum of A and B valences is 7. The oxygen can be replaced in part by sulfur or fluorine. Typical pyrochlores which we believe to have potential as thermal barrier coatings are those in which A is selected from the group consisting of lanthanum, gadolinium and yttrium and mixtures thereof (the present invention being limited to gadolinium and single phase mixtures of gadolinium with lanthanum and/or yttrium) and B is selected from the group consisting of zirconium, hafnium and titanium and mixtures thereof. Many other pyrochlores exist which also have potential as thermal barrier metals. See "Oxide Pyrochlores - A Review" by M. A. Subramanian et al, Progress in Solid State Chemistry, vol 15, pp 55-143, 1983 for a full description of pyrochlores.

15 [0016] We have found that on a density adjusted basis pyrochlores which we have investigated have thermal insulating properties which exceed those of the more commonly used zirconia based thermal barrier materials. Additionally many of the pyrochlore materials have a phase relationship in which the pyrochlore structure is phase stable up to the melting point. Consequently stabilizing additions are not required. Most of the pyrochlores which we have investigated have melting points of more than 1650 °C (3000 °F) and generally more than 2200 °C (4000 °F). Additionally these materials adhere to alumina. These are all properties which are useful in thermal barrier coatings.

20 [0017] The invention coating materials and coatings will usually be used to protect a superalloy substrate from excess temperatures. Superalloys are metals, usually based on iron, nickel or cobalt and containing chromium and aluminum and usually titanium and refractory metals, and having useful properties above 650°C (1200°F). Other substrates, 25 including steels, copper alloys and titanium alloys may be protected. Table I describes exemplary substrate materials.

TABLE I

(wt % Exemplary Superalloy Compositions)														
	Cr	Co	W	Cb	Ti	Al	B	Hf	C	Ni	Ta	Mo	Zr	Re
PWA1422	9	10	12	1	2	5	0.015	1.6	0.14	Bal	-	-	-	-
PWA1426	6.4	12.6	6.4	-	-	5.9	0.012	1.5	-	Bal	3.0	1.7	0.08	0.3
PWA1480	10	5	4	-	1.5	5	-	-	-	Bal	12	-	-	-
IN 792	12	9	3.8	-	4.1	3.5	.015	0.5	0.12	Bal	3.9	1.9	0.12	-

40 [0018] As in other ceramic thermal barrier coatings, adherence of the pyrochlore ceramic to the alloy substrate is critical.

45 [0019] It is known from prior zirconia thermal barrier coatings that a metallic bond coat (sometimes described as an overlay coating) such as a MCrAlY is a superior bond coat for oxide ceramic coatings. It is also known that aluminide coatings are useful bond coats through generally not as durable as MCrAlY bond coats. The common feature of overlay coatings and aluminide coatings is that they both form adherent alumina surface films or scales.

50 [0020] A broad composition range for MCrAlY materials is 10-25% Cr, 5-15 Al, .1-1.0 Y balance selected from Fe, Ni, and Co and mixtures of Ni and Co. Additions of up to 5% each of Hf, Ta or Re, up to 1% of Si and up to 3% each of Os, Pt, Pd, or Rh may also be made. Table II describes exemplary MCrAlYs that can be applied by thermal spray processes, by EBPVD processes, and by electroplating.

TABLE II

(wt % Exemplary MCrAlY Compositions)							
	Ni	Co	Cr	Al	Y	Hf	Si
MCrAlY	Bal	-	19.5	12.5	0.45	-	-
CoCrAlY	-	Bal	18	11	0.45	-	-
NiCoCrAlY	Bal	23	18	12.5	0.3	-	-

TABLE II (continued)

(wt % Exemplary MCrAlY Compositions)								
	Ni	Co	Cr	Al	Y	Hf	Si	
	NiCoCrAlY	Bal	22	17	12.5	0.6	0.25	0.4

- [0021] An alternate bond coat is a diffusion aluminide formed by diffusing aluminum into the substrate surface. Diffusion aluminides are well known and may be applied using a mixture (termed a pack) containing an aluminum source, such as an aluminum alloy or compound, an activator (usually a halide compound such as NaF) and an inert material such as alumina. The part to be coated is buried in the pack and heated to 816-1094°C (1500-2000°F) while a carrier gas, such as hydrogen, is flowed through the pack. Out of pack processes wherein the part is not buried in the pack are also known. The incorporation of precious metals such as Pt, Rh, Pd and Os into aluminide coatings is known. See US patent 5,514,482 for a description of aluminide coating processes.
- [0022] Combinations of overlay and aluminide coatings are also possible. See US patent 4,897,315 for a description of a system having an inner MCrAlY overlay coating and an outer aluminide coating. See US patent 4,005,989 for a description of the reverse combination, an inner aluminide coating and an outer overlay coating.
- [0023] The common feature of these bond coats and bond coat combinations is that they form an adherent layer of alumina on their outer surface. The invention thermal barrier coating has limited solubility in alumina but bonds firmly to the alumina.
- [0024] In certain cases, superalloys may form sufficiently perfect and adherent alumina layers that ceramics may adhere without a separate bond coat. See US patents 5,262,245, 4,895,201, 5,034,284, 5,346,563, and 5,538,796.
- [0025] To date all successful applications of ceramic coatings to superalloy has included oxide layer (usually alumina, rarely silica) between the bond coat (or substrate) and the ceramic coating.
- [0026] Certain preferred embodiments will now be described by way of example only and with reference to the accompanying drawings, in which

FIG. 1a depicts the crystal structure of lanthanum zirconate (which material is outside the scope of the present invention), a pyrochlore;
 FIG. 1b depicts the crystal structure of zirconia, a fluorite structure;
 FIG. 2 shows the relationship between the A and B constituent ionic sizes necessary to produce a pyrochlore structure;
 FIG. 3a depicts a ceramic coating directly on a metallic substrate;
 FIG. 3b depicts a ceramic coating on a metallic substrate with an intermediate bond coat;
 FIG. 3c depicts an expanded view of the interface between the bond coat and the ceramic layer in FIG. 3b;
 FIG. 4 shows the ZrO_2 - La_2O_3 phase diagram;
 FIG. 5 shows the thermal conductivity of several ceramic materials ;
 FIG. 6 shows the coefficient of thermal expansion for several ceramic materials; and
 FIG. 7 shows an X-ray diffraction scan from the surface of a preferred coating.

- [0027] The pyrochlore structure is a complex structure which can be described in a variety of ways, as a fluorite structure derivative, or as a network of octahedrals linked corner to corner with cations filling the interstices.
- [0028] Fig. 1a is a depiction of a cubic pyrochlore crystal structure. Regardless of structure description the pyrochlore structure has a chemical composition of $A_2 B_2 O_7$ or occasionally $A_2 B_2 O_6$ or $AB_2 O_6$ with the latter two being referred to as defect pyrochlores. Fig. 1a illustrates lanthanum zirconate (which is not a material of the present invention) having an $A_2B_2O_7$ chemistry. Fig. 1b shows a cubic fluorite structure, the structure of stabilized zirconia. A comparison of Figs. 1a and 1b shows both similarities and differences between the two structures. Both Figs. 1a and 1b are views down the <100> crystal axis. Visually the pyrochlore structure appears to be less regular than the fluorite structure.
- [0029] The A and B ions can have different valences as long as the sum of the A and B valences adds up to 7, in the case of the $A_2, B_2 O_7$ or 6 in the case of $A_2B_2O_6$ structures.
- [0030] The pyrochlore structure forms only for certain relationships of A and B ionic radii. Fig. 2 illustrates this relationship indicating the general combination of A and B ionic radii which produce cubic pyrochlores. We have found that the boundaries of this diagram are somewhat uncertain and we believe, based on our investigations, that lanthanum titanate [$La_2 Ti_2 O_7$], through outside the scope of the present invention, has a stable cubic pyrochlore structure.
- [0031] Noncubic pyrochlores are known but for the purpose of this invention we use ceramics which have a cubic pyrochlore structure.
- [0032] As shown in Fig. 2, the formation of the desired cubic pyrochlore crystal structure is controlled by the relative ionic radii of the A and B constituents. It is possible to use a mixture of elements for the A and/or B constituents to

provide an average ionic radius which will cause formation of a cubic pyrochlore structure. By way of example, from Fig. 2 it can be seen that both $Gd_2Ti_2O_7$ and $Y_2Zr_2O_7$ will have cubic pyrochlore structures. As a general rule, compounds of the formula $(Gd_xY_y)(Ti_aZr_b)O_7$, where $x+y = 2$ and $a+b = 2$, will also have a cubic pyrochlore structure.

[0033] Further, a compound such as $In_2Zr_2O_7$ (which is not within the present invention) which is not cubic could likely be rendered cubic through partial substitution of (for example) Nd for In and/or Ti for Zr, to bring the average A and B ionic radii into the cubic pyrochlore region shown in Fig. 2.

[0034] We have worked with the type of pyrochlores denoted by the $A_2B_2O_7$ formula and of these we use gadolinium for the A ionic species and hafnium, titanium or zirconium for the B ionic species.

[0035] Ti, Zr and Hf all display complete solid solubility in each other and we believe that any combination of Ti + Zr + Hf can be used as the B ionic species. Similarly, Gd, La and Y have substantial solid solubilities (Gd - La has complete solubility). Any combination of La + Y which does not form a second phase in Gd can be used as the A ionic species. These alloys of the A and B species must satisfy the criteria of Fig. 2 and possess a pyrochlore structure.

[0036] The low thermal conductivity of oxide pyrochlore compounds can be rationalized by consideration of crystallographic and chemical effects on thermal conductivity. The thermal conductivity of dielectric solids at elevated temperature is determined by phonon scattering by crystal imperfections and other phonons. Oxide pyrochlore compounds exhibit many of the features associated with low thermal conductivity materials. The pyrochlore crystal structure has a high intrinsic defect concentration. It has been experimentally established that as the difference in atomic mass between constituents in a compound increases, the thermal conductivity of that compound tends to decrease. Although the pyrochlore and fluorite structure are closely related, substitution of a high concentration of high atomic mass atoms (lanthanum, gadolinium and yttrium) into the fluorite structure provides a means to lower thermal conductivity that does not readily exist with stabilized zirconia compounds. It should be noted that, for thermal barrier applications, the benefits obtained from the reduction in thermal conductivity resulting from the use of high atomic mass elements must out weigh the debit incurred from higher density.

[0037] Reduction in thermal conductivity has also been associated with increasing complexity of crystallographic structure. As shown in Fig. 1a, the pyrochlore structure exhibits a greater degree of complexity than the fluorite structure shown in Fig. 1b. The cubic pyrochlore structure is similar to the cubic fluorite structure but with a large number of the oxygen atoms displaced (and one in eight missing).

[0038] Thermal barrier coatings are typically applied by thermal spray processes, such as plasma spray, in air (APS) or in low pressure (LPPS) by high velocity oxygen fuel processes (HVOF) or by detonation guns (D Gun). Electron beam physical vapor deposition (EBPVD) and sputtering are other techniques. Electron beam physical vapor deposition is a favored process. Depending upon the application and circumstances, each process has particular advantages. All of these processes can be readily used to apply oxide pyrochlore thermal barrier coatings. As previously discussed, the EBPVD process offers advantages since it develops a structure suited for extreme temperature applications and is therefore be most suitable for coating hot section turbine components. Thermal spray processing offers advantages in coating large components of complex shape and would be most suitable in coating components such as combustors.

[0039] Figs. 3a, b and c illustrates variants of the thermal barrier coatings of the present invention. Fig. 3a depicts a coated article which comprises a superalloy substrate 10 having a pyrochlore top coat 20 on its outer surface 21. In gas turbine applications the backside 11 of the superalloy substrate 10 will be cooled by cooling air (not shown) and the outside front surface 21 of the pyrochlore will be exposed to elevated temperatures. There may also be holes between the outer surface and the backside permitting cooling air to flow from the backside to the outer surface. Angled and shaped cooling holes in combination with flowing hot gases on the outer surface can produce film cooling in which a layer of cool air separates the outside surface from the hot gases to further reduce heat flow. Heat will flow from the front surface 21 to the cooled surface 11 and the quantity of the heat flow will be substantially reduced by the pyrochlore layer. As previously mentioned the pyrochlore may be applied by various methods and the macrostructure of the pyrochlore layer will be largely a function of the deposition process. The most basic invention embodiment is a pyrochlore layer adhered to a substrate which reduces heat flow in the presence of a thermal gradient.

[0040] Fig. 3b illustrates a preferred construction which employs a bond coat 15 between the substrate 10 and the pyrochlore 20. The bond coat 15 improves adherence and provides oxidation protection for the substrate. Fig. 3c is an expanded view of the interlayer 16 between the bond coat 15 and the pyrochlore layer 20. An oxide layer 22, principally of alumina, exists at this interlayer and is believed to be principally responsible for the adherence of the pyrochlore.

[0041] It is known to augment the naturally occurring alumina layer on the bond coat by sputtering alumina onto the bond coat, in the case of zirconia thermal barrier coatings, and the use of a separately applied alumina layer (rather than a thermally grown oxide layer) is also an embodiment of this invention.

[0042] In a further embodiment another ceramic layer may be applied to the free surface of the pyrochlore. This added layer can be selected to reduce oxygen diffusion, to provide erosion and abrasion resistance, or to provide a desired thermal emissivity characteristic, or some combination of these characteristics.

Example I

[0043] The use of the $\text{La}_2\text{Zr}_2\text{O}_7$ (lanthanum zirconate) pyrochlore oxide compound as a EBPVD applied thermal barrier coating will be illustrated. While not an embodiment of the present invention, its use is illustrative of a pyrochlore material based on gadolinium. The advantageous properties of the $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore oxide relative to stabilized zirconia for thermal barrier coating include thermal conductivity, thermal expansion, density, and phase stability. Fig. 4 shows the La_2O_3 - ZrO_2 phase diagram with the pyrochlore phase field labeled P. It can be seen that the pyrochlore structure (at about 35 mol % La_2O_3) is stable up to the melting point at about 2300 °C (4172 °F).

[0044] Fig. 5 shows thermal conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$ compared to the thermal conductivity of cubic zirconia as a function of temperature. At typical thermal barrier coating use temperatures, the pyrochlore compound exhibits a thermal conductivity which is about 50% that of stabilized zirconia. The density of the $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore compound is approximately the same as stabilized zirconia (approximately $69/\text{cm}^3$) so on a weight corrected basis, the thermal conductivity benefit is also about 50%.

[0045] To illustrate the benefit, the 50 percent reduction thermal conductivity allows the coating thickness to be reduced by 50 percent for the same degree of thermal protection. Decreasing the coating mass by 50 percent on a typical turbine blade will lower the blade pull at the blade root by approximately 680 Kg (1,500 pounds), at typical operating conditions, which results in a significant increase in blade life and permits a reduction in mass of the disk to which the blades are attached. If the thermal barrier coating were held at the same thickness, and the cooling air flow held constant, the substrate temperature would be reduced by about 55 °C (100 °F), giving increased substrate creep life.

[0046] Keeping the coating thickness constant and reducing the airflow would increase engine efficiency.

[0046] Fig. 6 shows the mean coefficient of thermal expansion of $\text{La}_2\text{Zr}_2\text{O}_7$ compared to that of cubic stabilized zirconia as a function of temperature. The thermal expansion of $\text{La}_2\text{Zr}_2\text{O}_7$ thermal barrier coating can be seen to be similar to that of the cubic zirconia thermal barrier coating. This means that $\text{La}_2\text{Zr}_2\text{O}_7$ will behave similarly to zirconia during thermal cycling.

Example II

[0047] Lanthanum zirconate was applied to a substrate by electron beam vapor deposition (EBPVD), in a controlled atmosphere chamber. Again, while the material is outside the scope of the present invention, this provides an illustration of a thermal spray technique for a ceramic pyrochlore coating. The coating was applied to a single crystal substrate (of the nominal composition of PWA 1480 (see Table II)). The coating process was carried out in a vacuum of 4.3×10^{-2} Pa (3.2×10^{-4} Torr) with an oxygen flow rate of 50 seem (8.33×10^{-7} m^3/s at specified standard temperature and pressure). Oxygen was added to ensure pyrochlore oxygen stoichiometry, see U.S. Patent 5,087,477. The substrate temperature was 1005°C (1840°F) during deposition with a substrate to source distance of 135mm (5.25 inches). The source pyrochlore ceramic was evaporated with an electron beam run at 0.8 A and 10,000 V. The source oxide was $\text{La}_2\text{Zr}_2\text{O}_7$ powder. The coating exhibited the favorable columnar grain structure typical of electron beam physical vapor deposited cubic zirconia thermal barrier coatings that provides strain relief and improved durability over plasma sprayed coatings.

[0048] Fig. 7 shows an X-ray diffraction scan obtained from the surface of the coating. The diffraction peaks have been indexed to the pyrochlore crystal structure which demonstrates that the pyrochlore structure was formed in the deposited thermal barrier coating.

Claims

1. A metallic article comprising a metallic substrate (10), said substrate having a ceramic coating (20) which has a cubic pyrochlore structure of formula $\text{A}_2\text{B}_2\text{O}_7$, wherein the A constituent consists essentially of Gd, and single phase mixtures of Gd with La and/or Y, and the B constituent is selected from Hf, Ti, Zr, and single phase mixtures thereof.
2. An article as claimed in claim 1, wherein said metallic article has an oxide scale on its outer surface, said oxide consisting substantially of alumina, and wherein said pyrochlore ceramic coating (20) is bonded to said oxide scale.
3. An article as claimed in claim 1, wherein said metallic substrate (10) is provided with an alumina forming coating (15) on its surface and the pyrochlore coating (20) is bonded to said alumina forming coating.
4. An article as claimed in claim 3, wherein said substrate coating (20) comprises an alumina forming metallic overlay coating.

5. An article as claimed in claim 3, wherein said substrate coating (20) comprises a diffusion aluminide coating.
6. An article as claimed in any of the preceding claims, wherein said metallic substrate (10) is selected from the group consisting of steels, superalloys, titanium alloys and copper alloys.
- 5 7. An article as claimed in any of the preceding claims, wherein said coated article is adapted to be used in environments where the free surface (21) of the pyrochlore coating (20) will be heated and the free surface (11) of the substrate (10) will be cooled, whereby the pyrochlore coating will reduce heat flow.
- 10 8. An article as claimed in any of the preceding claims, wherein said pyrochlore coating has a columnar microstructure.
9. An article as claimed in any of the preceding claims, wherein another ceramic layer is provided on the free surface (21) of the pyrochlore ceramic coating (20).
- 15 10. A superalloy gas turbine component (10) which operates in an environment with gas temperatures in excess of 1,000°C, said component having internal cooling passages, wherein said component comprises a metallic article as claimed in any of the preceding claims, wherein said pyrochlore coating is located to reduce heat flow into said component.
- 20 11. A method of thermally insulating a metallic substrate (10) which comprises applying a thermal barrier layer in the form of a ceramic coating (20) to at least a portion of said substrate by electron beam physical vapor deposition or thermal spray deposition, the ceramic coating having a cubic pyrochlore structure of formula $A_2B_2O_7$, wherein the A constituent consists essentially of Gd, and single phase mixtures of Gd with La and/or Y, and the B constituent is selected from the group comprising Hf, Ti, Zr and single phase mixtures thereof.
- 25 12. A method as claimed in claim 11, wherein said pyrochlore material is applied directly to the surface of said metallic substrate.
13. A method as claimed in claim 11, wherein an alumina forming coating is applied on the surface of said metallic substrates and said pyrochlore coating is bonded to said alumina forming coating.
- 30 14. A method as claimed in claim 13, wherein said alumina forming coating comprises a metallic overlay coating.
15. A method as claimed in claim 13, wherein said alumina forming coating comprises a diffusion aluminide coating.
- 35 16. A method as claimed in any of claims 11 to 15, wherein said pyrochlore coating is formed with a columnar micro-structure.
17. A method as claimed in any of claims 11 to 16, wherein said metallic substrate is selected from the group consisting of steels, superalloys, titanium alloys and copper alloys.
- 40 18. A method as claimed in any of claims 11 to 17, wherein another ceramic layer is applied to the free surface of the pyrochlore ceramic coating (20).

- 45 **Patentansprüche**
1. Metallischer Gegenstand aufweisend ein metallisches Substrat (10), das eine Keramikbeschichtung (20) besitzt, die eine kubische Pyrochlor-Struktur der Formel $A_2B_2O_7$ hat, wobei der Bestandteil A im Wesentlichen aus Gd und einphasigen Gemischen von Gd mit La und/oder Y besteht und der Bestandteil B aus Hf, Ti, Zr und einphasigen Gemischen davon ausgewählt ist.
- 50 2. Gegenstand nach Anspruch 1, bei dem der metallische Gegenstand an seiner Außenoberfläche einen Oxidbelag hat, wobei das Oxid im Wesentlichen aus Aluminiumoxid besteht, und bei dem die Pyrochlor-Keramikbeschichtung (20) an dem Oxidbelag haftet.
- 55 3. Gegenstand nach Anspruch 1, bei dem das metallische Substrat (10) an seiner Oberfläche mit einer Aluminiumoxid bildenden Beschichtung (15) ausgestattet ist und die Pyrochlor-Beschichtung (20) an der Aluminiumoxid bildenden

Beschichtung haftet.

4. Gegenstand nach Anspruch 3, bei dem die Substratbeschichtung (20) eine Aluminiumoxid bildende metallische Auflagebeschichtung aufweist.
5. Gegenstand nach Anspruch 3, bei dem die Substratbeschichtung (20) eine Diffusions-Aluminidbeschichtung aufweist.
10. Gegenstand nach einem der vorangehenden Ansprüche, bei dem das metallische Substrat (10) ausgewählt ist aus der Gruppe, die aus Stählen, Superlegierungen, Titanlegierungen und Kupferlegierungen besteht.
15. Gegenstand nach einem der vorangehenden Ansprüche, bei dem der beschichtete Gegenstand dazu geeignet ist, in Umgebungen verwendet zu werden, in denen die freie Oberfläche (21) der Pyrochlor-Beschichtung (20) erhitzt wird und die freie Oberfläche (11) des Substrats (10) gekühlt wird, wobei die Pyrochlor-Beschichtung den Wärmefluss verringert.
20. Gegenstand nach einem der vorangehenden Ansprüche, bei dem die Pyrochlor-Beschichtung eine säulenförmige Mikrostruktur hat.
25. Gegenstand nach einem der vorangehenden Ansprüche, bei dem an der freien Oberfläche (21) der Pyrochlor-Keramikbeschichtung (20) eine weitere Keramikschicht vorgesehen ist.
30. Gastubinenbauteil (10) aus Superlegierung, das in einer Umgebung mit Gastemperaturen oberhalb 1000°C arbeitet, wobei das Bauteil innere Kühl durchlässe hat, wobei das Bauteil einen metallischen Gegenstand nach einem der vorangehenden Ansprüche aufweist, wobei die Pyrochlor-Beschichtung zur Verringerung des Wärmeflusses in den Bestandteil angebracht ist.
35. Verfahren zum thermischen Isolieren eines metallischen Substrats (10), das das Aufbringen einer Wärmesperrschicht in Form einer Keramikbeschichtung (20) auf mindestens einen Teil des Substrats durch physikalische Dampfabscheidung mittels Elektronenstrahl oder durch Abscheidung mittels thermischen Spritzens aufweist, wobei die Keramikbeschichtung eine kubische Pyrochlor-Struktur der Formel $A_2B_2O_7$ hat, worin der Bestandteil A im Wesentlichen aus Gd und einphasigen Gemischen von Gd mit La und/oder Y besteht und der Bestandteil B ausgewählt ist aus der Hf, Ti, Zr und einphasige Gemische davon aufweisenden Gruppe.
40. Verfahren nach Anspruch 11, bei dem das Pyrochlor-Material direkt auf die Oberfläche des metallischen Substrats aufgebracht wird.
45. Verfahren nach Anspruch 11, bei dem eine Aluminiumoxid bildende Beschichtung auf die Oberfläche des metallischen Substrats aufgebracht wird und die Pyrochlor-Beschichtung an die Aluminiumoxid bildende Beschichtung gebunden wird.
50. Verfahren nach Anspruch 13, bei dem die Aluminiumoxid bildende Beschichtung eine metallische Auflagebeschichtung aufweist.
55. Verfahren nach Anspruch 13, bei dem die Aluminiumoxid bildende Beschichtung eine Diffusions-Aluminidbeschichtung aufweist.
16. Verfahren nach einem der Ansprüche 11 bis 15, bei dem die Pyrochlor-Beschichtung mit einer säulenförmigen Mikrostruktur ausgebildet wird.
17. Verfahren nach einem der Ansprüche 11 bis 16, bei dem das metallische Substrat ausgewählt wird aus der aus Stählen, Superlegierungen, Titanlegierungen und Kupferlegierungen bestehenden Gruppe.
18. Verfahren nach einem der Ansprüche 11 bis 17, bei dem auf die freie Oberfläche der Pyrochlor-Keramikbeschichtung (20) eine weitere Keramikschicht aufgebracht wird.

Revendications

1. Article métallique comprenant un substrat métallique (10), ledit substrat ayant un revêtement céramique (20) qui a une structure de pyrochlore cubique de formule $A_2B_2O_7$, dans laquelle le constituant A consiste essentiellement en Gd, et en mélanges à une seule phase de Gd avec La et/ou Y, et le constituant B est choisi parmi Hf, Ti, Zr et leurs mélanges à une seule phase.
2. Article selon la revendication 1, dans lequel ledit article métallique a une couche d'oxyde sur sa surface extérieure, ledit oxyde étant constitué principalement d'alumine, et dans lequel ledit revêtement céramique de type pyrochlore (20) est collé à ladite couche d'oxyde.
3. Article selon la revendication 1, dans lequel ledit substrat métallique (10) est muni d'un revêtement (15) formant de l'alumine sur sa surface et le revêtement de pyrochlore (20) est lié audit revêtement formant de l'alumine.
4. Article selon la revendication 3, dans lequel ledit revêtement de substrat (20) comprend un revêtement de finition métallique formant de l'alumine.
5. Article selon la revendication 3, dans lequel ledit revêtement de substrat (20) comprend un revêtement à diffusion d'aluminiure.
6. Article selon l'une quelconque des revendications précédentes, dans lequel ledit substrat métallique (10) est choisi dans le groupe constitué par les aciers, les superalliages, les alliages de titane et les alliages de cuivre.
7. Article selon l'une quelconque des revendications précédentes, dans lequel ledit article revêtu est adapté pour être utilisé dans des environnements où la surface libre (21) du revêtement de pyrochlore (20) va être chauffée et la surface libre (11) du substrat va être refroidie, en conséquence de quoi le revêtement de pyrochlore va réduire le flux de chaleur.
8. Article selon l'une quelconque des revendications précédentes, dans lequel ledit revêtement de pyrochlore a une microstructure en colonnes.
9. Article selon l'une quelconque des revendications précédentes, dans lequel une autre couche de céramique est prévue sur la surface libre (21) du revêtement céramique de pyrochlore (20).
10. Composant de turbine à gaz en superalliage (10) qui opère dans un environnement avec des températures de gaz dépassant 1000°C, ledit composant ayant des passages de refroidissement internes, dans lequel ledit composant comprend un article métallique selon l'une quelconque des revendications précédentes, dans lequel ledit revêtement de pyrochlore est localisé de façon à réduire le flux de chaleur dans ledit composant.
11. Procédé pour isoler thermiquement un substrat métallique (10), qui comprend l'application d'une couche formant barrière thermique sous la forme d'un revêtement céramique (20) à au moins une partie dudit substrat par déposition physique en phase vapeur par faisceau d'électrons ou déposition par pulvérisation thermique, le revêtement céramique ayant une structure de pyrochlore cubique de formule $A_2B_2O_7$, dans laquelle le constituant A consiste essentiellement en Gd, et en mélanges à une seule phase de Gd avec La et/ou Y, et le constituant B est choisi parmi Hf, Ti, Zr et leurs mélanges à une seule phase.
12. Procédé selon la revendication 11, dans lequel ledit matériau pyrochlore est appliqué directement sur la surface dudit substrat métallique.
13. Procédé selon la revendication 11, dans lequel un revêtement formant de l'alumine est appliqué sur la surface desdits substrats métalliques et ledit revêtement de pyrochlore est collé audit revêtement formant de l'alumine.
14. Procédé selon la revendication 13, dans lequel ledit revêtement formant de l'alumine comprend un revêtement de finition métallique.
15. Procédé selon la revendication 13, dans lequel ledit revêtement formant de l'alumine comprend un revêtement à diffusion d'aluminiure.

16. Procédé selon l'une quelconque des revendications 11 à 15, dans lequel ledit revêtement de pyrochlore est formé avec une microstructure à colonnes.
17. Procédé selon l'une quelconque des revendications 11 à 16, dans lequel ledit substrat métallique est choisi dans 5 le groupe constitué par les aciers, les superalliages, les alliages de titane et les alliages de cuivre.
18. Procédé selon l'une quelconque des revendications 11 à 17, dans lequel une autre couche de céramique est appliquée sur la surface libre du revêtement céramique de pyrochlore (20).

10

15

20

25

30

35

40

45

50

55

FIG. 1A

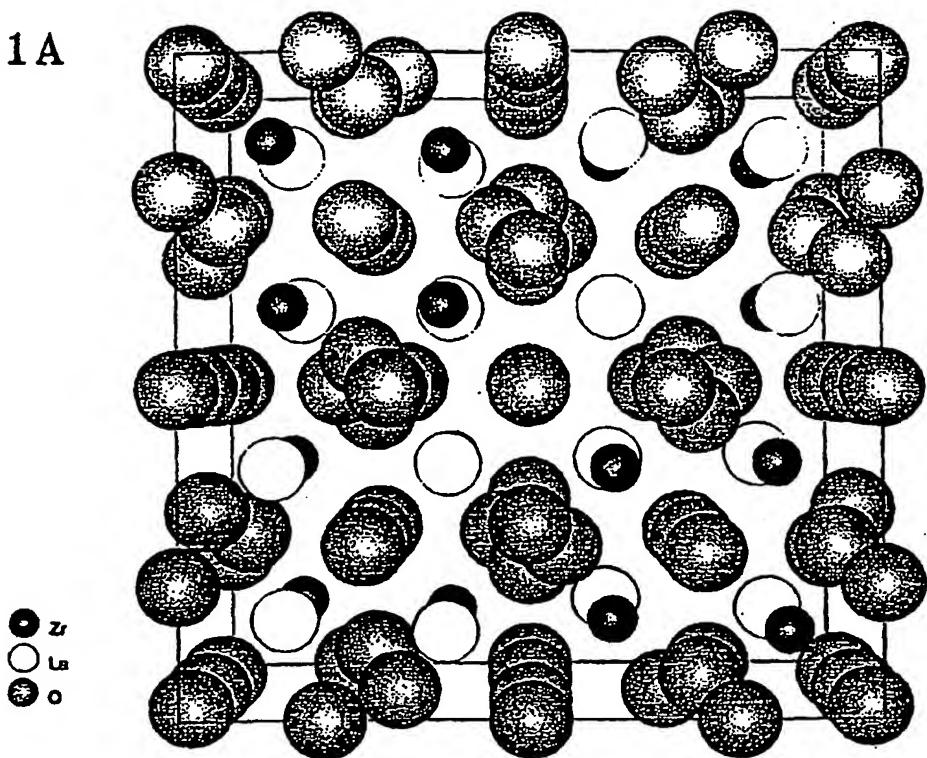


FIG. 1B

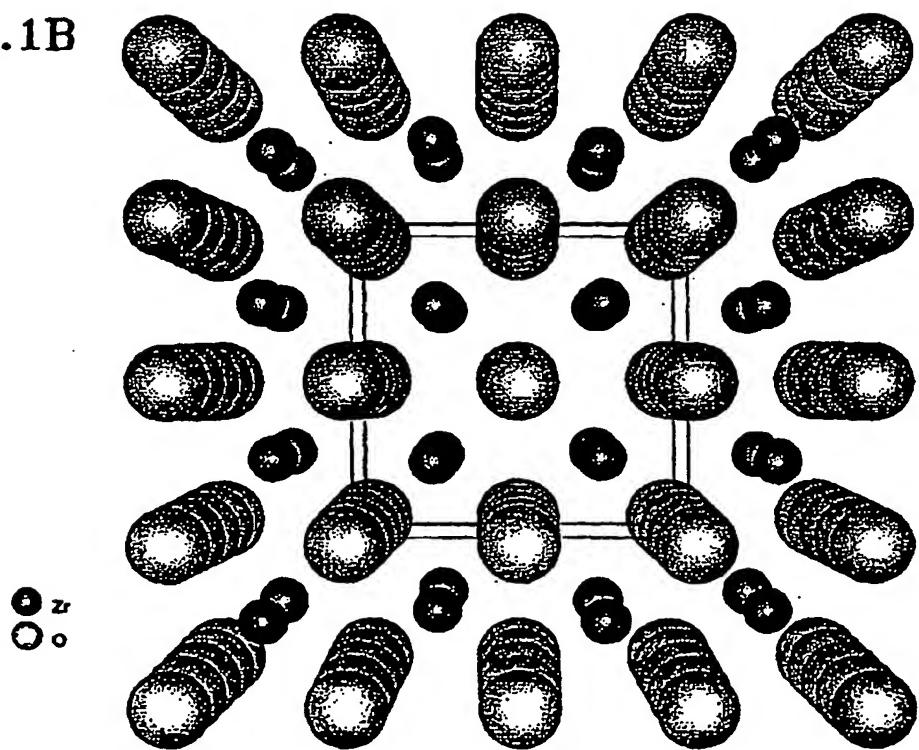


FIG. 2

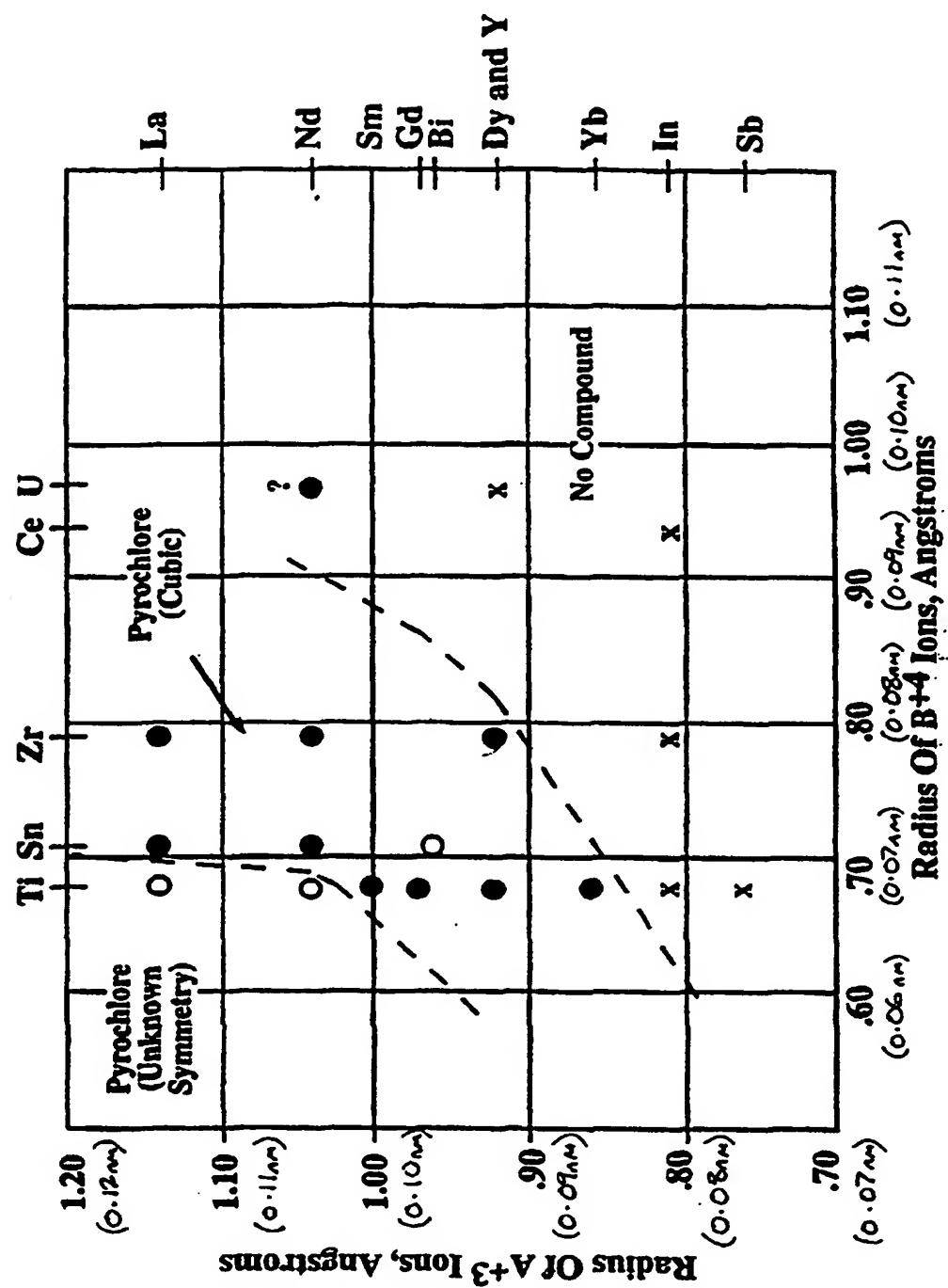


FIG.3A

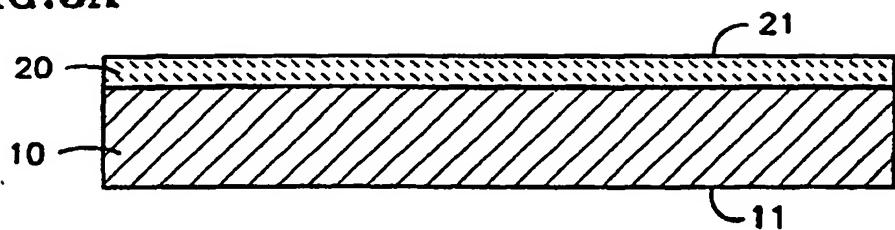


FIG.3B

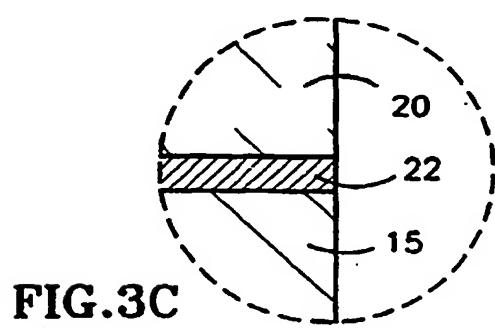
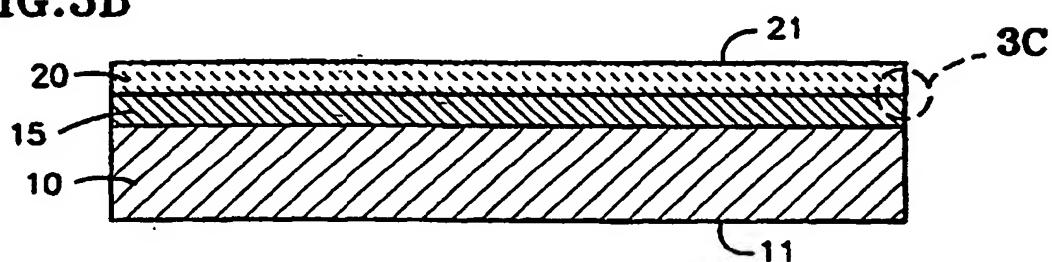
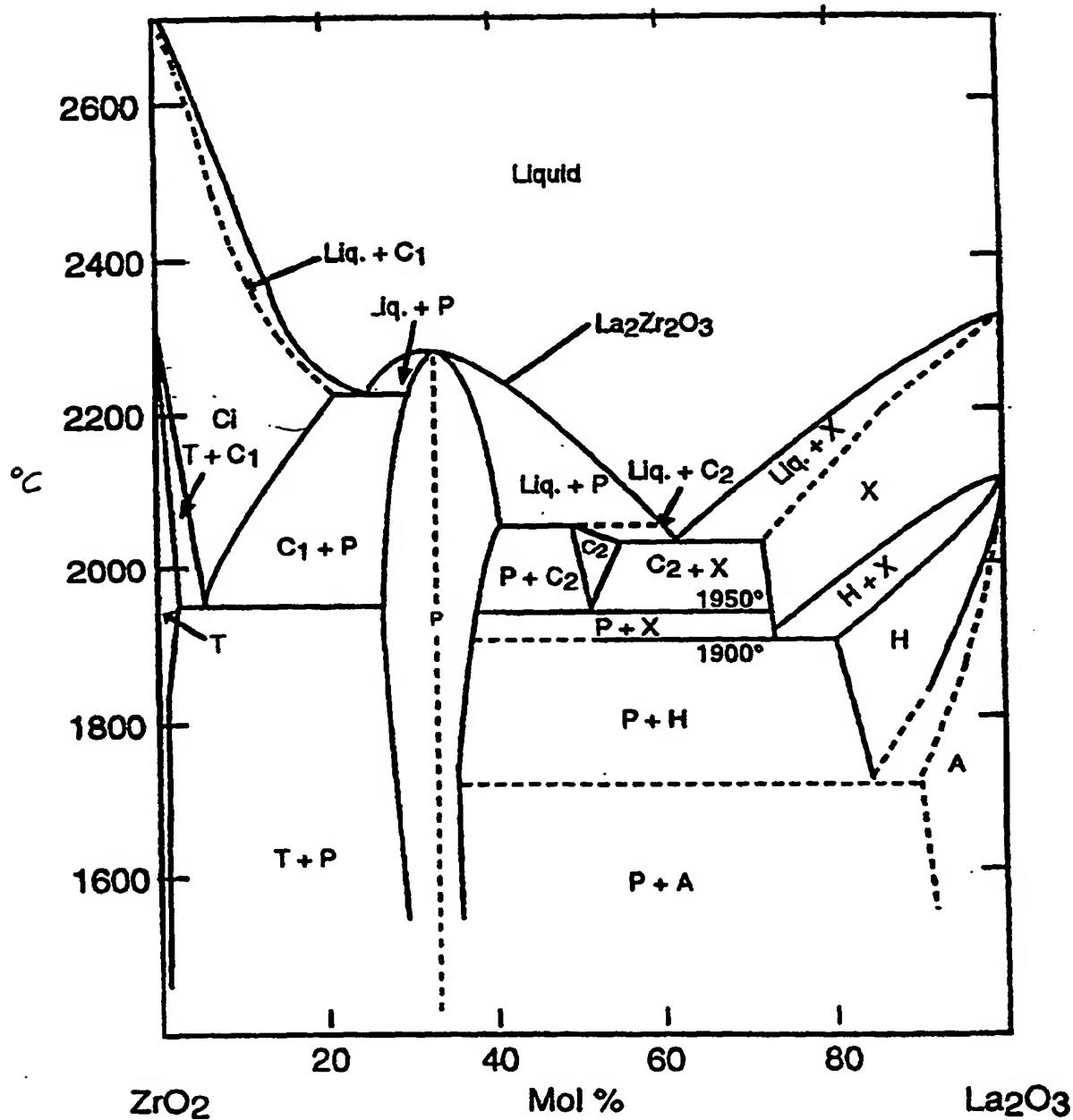


FIG.3C

FIG.4

 $\text{La}_2\text{O}_3\text{-ZrO}_2$ 

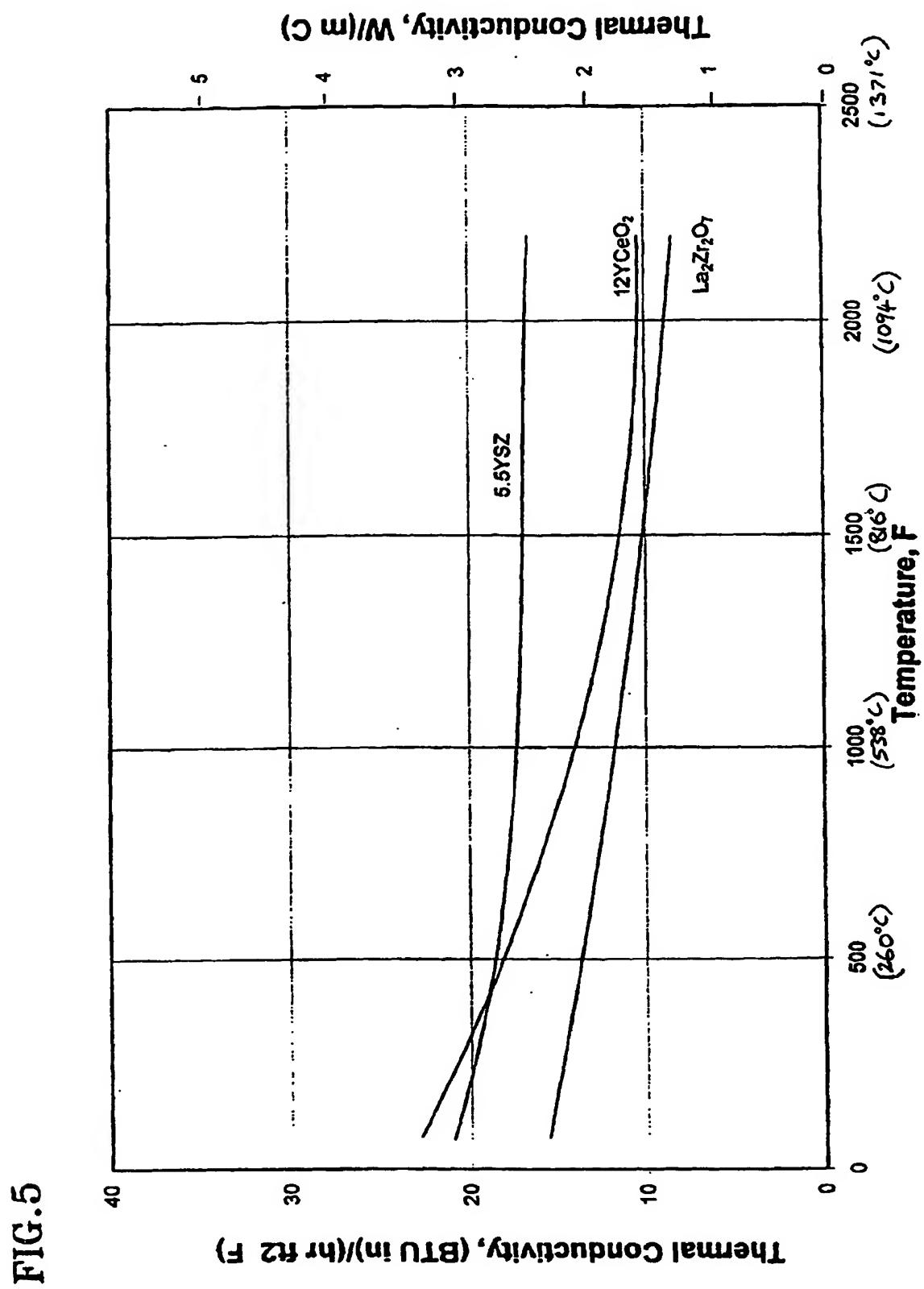


FIG. 6

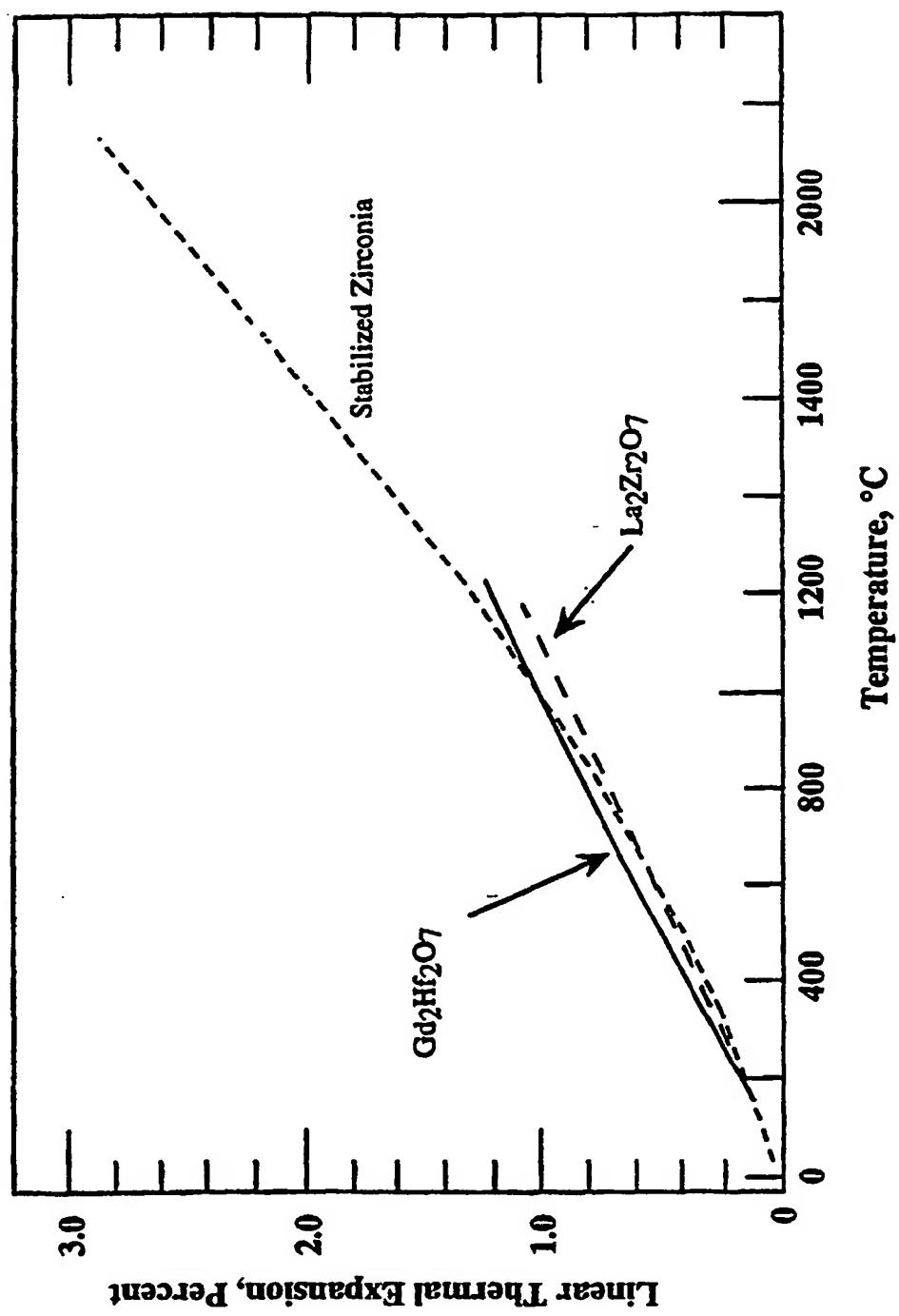


FIG. 7

